



Degradation of acetic acid by heterogeneous Fenton-like oxidation over iron-containing ZSM-5 zeolites



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ABSTRACT

In this study, the degradation of acetic acid was investigated by heterogeneous Fenton-like oxidation in the presence of iron-containing ZSM-5 zeolites. Iron content and Brønsted acidity of the catalyst affected positively and significantly the activity of catalyst in acetic acid (AA) degradation. The catalysts were prepared by ion-exchange method by using ZSM-5 type zeolites with different Si/Al ratio and characterized by XRD, SEM, FT-IR, ICP-AES and nitrogen adsorption measurements. The catalyst (IE-FeZSM-5 (90)) with Si/Al ratio of 42 and iron content of 8.5% (in wt) was found to be the most active catalyst in AA degradation. The influence of temperature, initial concentration of acid, amounts of H₂O₂ and catalyst and solution pH was investigated on degradation of AA by heterogeneous Fenton-like oxidation over this catalyst. Degradation of AA was accelerated at pH around 4 and temperature, H₂O₂ amount, catalyst loading and initial concentration of AA affected significantly the destruction of acid. The optimum conditions were obtained to be 0.2 g of catalyst, 333 K of temperature, solution pH of 4 and H₂O₂ amount of 8.35 mmol for an AA concentration of 0.1 g/dm³ with a COD removal of 50.5%. Degradation of AA obeyed first order kinetics with a rate expression of $-r_{AA} = 2.56 \times 10^7 e^{-61.5/RT} C_{AA}$ where $-r_{AA}$ in mol/dm³ min, R in kJ/mol.K, T in K and C_{AA} in mol/dm³.

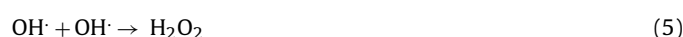
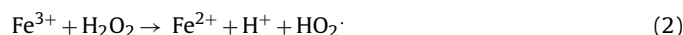
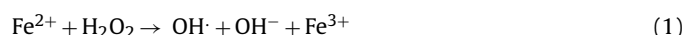
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1. Introduction

It is well known that water is an inevitable requirement for life and plays a vital role for human, animals and plants. Since the last two centuries, especially, after the Industrial Revolution, water rapidly includes lots of different toxic impurities originating from petrochemical, pharmaceutical, paper pulp and textile industries [1,2]. Due to these impurities that threatened natural life, wastewater treatment processes have become of great interest in the last few decades in the world.

Several conventional processes, including incineration, biological, physical and chemical, constitute mainly treatment processes of wastewater [3–6]. In chemical treatment approaches, advanced oxidation processes (AOPs) such as Fenton, photo-Fenton, ozonation and wet air oxidation attract considerable attention for destruction of various harmful organic pollutants [3,5,7–11]. Among these AOPs, Fenton's reagent seems to be a promising process for decomposition of non-biodegradable and recalcitrant organic pollutants [12]. Also, Fenton's reagent plays a key role in terms of simplicity of equipment, ambient conditions (atmospheric

pressure, low temperature), rapid oxidation rate, low investment cost and easy to operate and maintenance [7,11,13–15]. The combination of hydrogen peroxide (H₂O₂) and ferrous (Fe²⁺) constitutes the classical Fenton reaction. Fenton mechanism schematically is shown in Eqs. (1)–(7).



Hydrogen peroxide (H₂O₂, $E = 1.80 \text{ V}$) is one of the preferable oxidant due to non-selectivity, fast reaction kinetics, inexpensive, safe, high oxidation potential even at room temperature, easy to operate and harmless end product such as CO₂ and H₂O [13,16,17]. However, it should be pointed out that classical Fenton's reagent which is called as "homogeneous Fenton process" leads to some significant problems: (i) it needs a separation process, which leads

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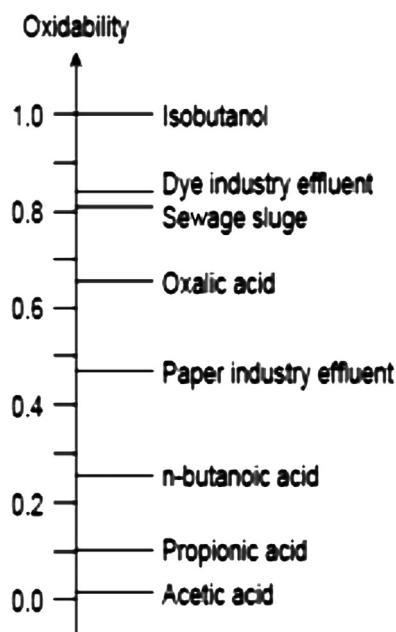


Fig. 1. Oxidability scale of various organic compounds under wet air oxidation, $T = 260^\circ\text{C}$, $P_{\text{O}_2} = 20$ bar, residence time = 1 h.

to spend more time, more reagents and high investment cost, at the end of the reaction to remove the iron ions, (ii) it requires narrow range of pH values (pH 2–4) for reaction and (iii) impossible regeneration of catalyst. To overcome these drawbacks of homogeneous Fenton process, heterogeneous catalysts in which iron is located in the porous solid structure have been developed. So, heterogeneous Fenton processes have been improved as a more practical and economical alternative to homogeneous Fenton process [1,2,4,7,9,12,14,16,18–20].

In this study, acetic acid was used as a model reactant. Acetic acid is commonly formed during the destruction of chemicals including longer chains of aliphatic acids or substances like phenol and phenolic compounds. It is resistant to oxidation due to the difficulty to oxidize the methyl group in α -position of the carboxylic group [16]. According to the Occupational Safety and Health Administration (OSHA), the legal permissible exposure limit of acetic acid is 10 mg/L and removal of acetic acid from wastewater is very important. Fig. 1 indicates the oxidability scale of the various organic substances under wet air oxidation [6]. This figure clearly shows how difficult the oxidation of acetic acid is even under severe conditions. There are a few studies on degradation of acetic acid (AA) by heterogeneous Fenton reaction. One of them is the study done by Larachi and co-workers [21]. In this study, wet oxidation of AA was investigated by H_2O_2 catalyzed by transition metal (Fe^{2+} , Fe^{3+} , Cu^{2+} , Mn^{2+})-exchanged NaY zeolites. They obtained a TOC removal of 63% at 90°C and 1 atm over Cu^{2+} -NaY zeolite catalyst. Centi and co-workers [16] achieved an AA conversion of 20% by wet peroxide oxidation over a Fe/ZSM-5 catalyst prepared by ion-exchange. However, their study was mainly on the oxidation of propionic acid, very little information was given on AA degradation. A destruction of 31% was reported by Karacan in catalytic wet air oxidation of AA over Pt/SiO₂ catalyst [22]. Sannino and co-workers [23,24] studied heterogeneous photo-Fenton oxidation of AA on supported LaFeO₃, LaMnO₃ and LnFeO₃ perovskites and they achieved TOC removal of 60, 54 and 100%, respectively, after an oxidation duration of 5 h.

However, so far, no study has been reported on the degradation of acetic acid by heterogeneous Fenton-like oxidation over FeZSM-5 zeolite catalysts. The specific objective of this paper is to investigate the removal efficiency of acetic acid in the presence

of iron-containing ZSM-5 zeolite catalysts using heterogeneous Fenton-like oxidation and the effects of several parameters such as temperature, initial concentration of acetic acid, solution pH, amounts of H_2O_2 and catalyst on the oxidation of acetic acid. It was aimed to describe the oxidation kinetics of acetic acid as well.

2. Experimental

2.1. Materials

ZSM-5 type zeolites (H-MFI) with different Si/Al ratio [H-MFI (27), H-Pentasil (45), H-MFI (55) and H-MFI (90)] were used in catalyst preparation by ion exchange method and were provided by Clariant-Süd-Chemie, Germany. Acetic acid (glacial, 100%) purchased from Merck was used without further purification process. The hydrogen peroxide solution (in mass % of 35) of analytical grade was obtained from Merck. All aqueous solutions containing 0.1 g/dm³ acetic acid were prepared with distilled water obtained from a Millipore Direct Q purification unit.

2.2. Catalyst preparation

In this study, four FeZSM-5 catalysts, IE-FeZSM-5 (90), IE-FeZSM-5 (55), IE-FeZSM-5 (45) and IE-FeZSM-5 (27), were prepared by using ion-exchange (IE) method. The method of Schwidder et al. [25] was applied with small differences for synthesis of the catalysts. To prepare the catalysts, 5 g of parent zeolite, 1.825 g of Fe powder (Riedel-de Haen AG) and 500 mL of deionized water were added into a double-necked flask equipped with a gas inlet–outlet tube and a magnetic stirrer. Later on, nitrogen was passed through the flask for 3 min and 4.14 mL of hydrochloric acid (in mass % of 37, J.T. Baker) was slowly charged into the mixture. After that, the mixture was stirred (at 250 rpm) under nitrogen atmosphere during 5 days. Ferrous ions are easily oxidized to corresponding ferric ions by oxygen in air, and the presence of nitrogen prevents this oxidation. So, pure Fe^{2+} solution could be obtained by reaction between iron powder and hydrochloric acid solution under the atmosphere of inert N_2 gas. After waiting for ion exchange for 2 days, it was filtered, and the obtained FeZSM-5 sample was washed with deionized water for 2.5 days (until no Cl^- detected in the washing water by controlling with 0.1 M AgNO_3 solution). The catalyst washed with deionized water was dried at room temperature for 4 days and calcined. For calcination, the catalyst dried was first heated to 423 K at a rate of 79 K/min and kept at this temperature for 15 min and then it was heated to 873 K at a rate of 47 K/min and kept at this temperature for 2 h. The prepared catalyst was called as IE-FeZSM-5 (90) or IE-FeZSM-5 (55) or IE-FeZSM-5 (45) or IE-FeZSM-5 (27) depending on the parent zeolite used.

2.3. Catalyst characterization

The crystalline structures of catalysts were determined by Shimadzu XRD-6000 model diffractometer (XRD) with $\text{Cu K}\alpha$ radiation. The scattering angle 2θ was varied from 2° to 80° with a scan rate of $0.02^\circ/\text{min}$. Current and voltage values were 30 mA and 40 kV, respectively. Morphological properties of the catalysts were analyzed by using scanning electron microscopy (SEM, FEI Quanta 250 FEG). The surface area, pore volume and average pore diameters of the catalysts were determined by nitrogen adsorption technique with Micromeritics ASAP 2010 equipment. Degassing was performed at 250°C for 3 h. Fourier transform infrared spectra (FT-IR) were saved in the 1700 – 400 cm^{-1} with a Perkin Elmer Spectrometer using KBr pellet technique. For this purpose, a typical pellet, containing 1 wt% of sample was prepared by mixing 2 mg of the sample with 200 mg of KBr. Metal contents and Si/Al ratios of all the catalysts and parent zeolites were determined by Thermo

Scientific iCAP 6500 inductively coupled plasma atomic emission spectrometer (ICP-AES) with fusion dissolution method. Fourier transform infrared spectroscopic studies of pyridine adsorbed on the catalysts prepared were made to distinguish between Brønsted and Lewis acids and to determine their amounts independently. For this purpose, from each sample 0.1 g was taken into flasks and 150 μl of pyridine was added onto each sample. The flasks were held closed for 12 h to let the pyridine adsorbed sufficiently on the surface. After that, vacuum was applied at 50 °C to the samples for 48 h to obtain monolayer coverage. FT-IR spectra of the pyridine-adsorbed catalysts were recorded by Perkin Elmer Spectrometer. FT-IR analysis took place at room temperature and atmospheric pressure.

2.4. Catalytic activity tests

The heterogeneous oxidative degradation of acetic acid (AA) by Fenton reaction was performed under isothermal conditions (333 K) in a shaded temperature-controlled glass batch reactor equipped with a mechanical stirrer at about 300 rpm (Heidolph) and a pH electrode (Mettler Toledo). For a typical run, 0.15 dm³ of acetic acid aqueous solution with a concentration of 0.10 g/dm³ was placed in the reactor and the temperature was adjusted to 333 K. After reaching the desired temperature, pH of the solution was measured and 0.15 g of catalyst (1.0 g/dm³) was added into the solution under continuous stirring. After stirring for 30 min, pH of the solution was again measured and the solution was analyzed in order to determine whether the acetic acid is adsorbed by the catalyst. Then a solution of 35% H₂O₂ (0.0557 M) was added to the 0.15 dm³ of acetic acid solution. After stirring the reaction mixture for 1 min, the pH of the solution was again measured and this time was recorded as the starting time of the reaction. At appropriate time intervals, about 2 mL samples were taken from the reaction mixture during the oxidation reaction. The samples taken were centrifuged for 20 min to remove the catalyst and the samples were used for COD analysis. Each run took 2 h.

For COD analysis, Lovibond Checkit Direct COD Vario device was used. Percentage COD removal was determined by Eq. (8). H₂O₂ consumption was measured by the Lovibond Hydrogen Peroxide PC_{CHECKIT}.

$$\text{COD removal \%} = \frac{\text{COD}_{\text{initial}} - \text{COD}_{t=t}}{\text{COD}_{\text{initial}}} \times 100 \quad (8)$$

Each run was repeated at least twice. Error bars were used in figures for the quantification of the experimental error. Standard deviation was reported for each set of runs.

3. Results and discussion

3.1. X-ray diffraction studies

Fig. 2 indicates the XRD patterns of the catalysts prepared by using ion-exchange method together with the parent zeolites for comparison. All the catalysts exhibited the typical diffractograms of the ZSM-5 zeolite (MFI framework) ($2\theta = 7-9^\circ$ and $23-25^\circ$) given in literature [26–38]. It is stressed that high dispersion of Fe ions in compensating positions inside zeolite did not damage the crystallinity of the zeolite. The addition of Fe ions into the structure of ZSM-5 zeolite decreases characteristic peak intensities of ZSM-5. This can be attributed to the enhanced absorption of X-ray due to Fe cations. The decrease in the peak intensities of the catalyst can depend on the reduction in crystal size of zeolite as a result of acid treatment and increase in the quantity of non-uniform regions formed by washing away aluminum from the zeolite structure, as well [28].

3.2. Scanning electron microscope (SEM) studies

Fig. 3 presents the morphology of prepared IE-FeZSM-5 catalyst samples and parent ZSM-5 zeolites. As shown in Fig. 3, different morphology is depicted for each catalyst sample prepared. The SEM images of IE-FeZSM-5 (90) and IE-FeZSM-5 (45) catalysts and their parent ZSM-5 zeolites showed that the crystallites were in the spherical shape with a spongy morphology. The SEM images of IE-FeZSM-5 (55) catalyst and its parent ZSM-5 zeolite indicated that the crystallites were as coffin-like shape. In the IE-FeZSM-5 (27) catalyst and its parent ZSM-5 zeolite the crystallites were in bar form and non-uniform in size. When the SEM images of IE-FeZSM-5 catalyst samples were compared with their parent ZSM-5 zeolites, it was seen that incorporation of iron cations into the zeolite structure could not be clearly observed. However, the presence of iron cation in the structure of prepared catalysts was confirmed by the inductively coupled plasma atomic emission spectrometer (ICP-AES) analysis.

3.3. Fourier transform infrared spectroscopy (FT-IR) studies

FT-IR spectra of prepared catalyst samples and the parent ZSM-5 zeolites were indicated in Fig. 4 in the range of 400–1700 cm^{−1}. All spectra indicated bands at 445, 550, 800, 1100, 1225 and 1650 cm^{−1} which were assigned to different vibrations of tetrahedral and framework structure of ZSM-5 zeolite associated with minor changes as a result of Fe incorporation. The bands at about 1100 and 445 cm^{−1} are due to the internal vibrations of (Si, Al, O₄) tetrahedral of ZSM-5, whereas the bands at 1225 and 800 cm^{−1} are due to vibrations related to external linkages between tetrahedral and hence sensitive to framework structure. The band at 550 cm^{−1} has been assigned to the five-membered ring of the pentasil zeolite structure [29,33,34].

3.4. Inductively coupled plasma atomic emission spectrometer (ICP-AES) studies

The composition of all the prepared catalysts and corresponding parent zeolites was determined by Thermo Scientific iCAP 6500 inductively coupled plasma atomic emission spectrometer (ICP-AES) with fusion dissolution method. Table 1 gives the results. As seen in Table 1, parent ZSM-5 zeolites include iron as impurity (7.5×10^{-4} wt%) in the crystal structure. The highest iron content was determined to be 8.5 wt% in IE-FeZSM-5 (90) catalyst. The Si/Al ratios of the iron containing zeolite catalysts measured via the ICP-AES analysis were found to be a little bit lower than those of the parent zeolites. This can be explained by the partial removal of Si from the zeolite framework (desilication) during the treatment.

3.5. Nitrogen adsorption studies

Table 1 also presents the BET surface area (S_{BET}), micropore area (S_{μ}), total pore volume (V_p), micropore volume (V_{μ}) and average pore diameter (d_{average} , calculated by Horvath–Kawazoe method) of prepared catalysts and parent zeolites. Iron loading to parent zeolites by ion-exchange method leads to a reduction in BET surface area except the IE-FeZSM-5 (90) catalyst. Average pore diameter of all the catalysts is around 0.6 nm except IE-FeZSM-5 (27).

3.6. Determination of Brønsted and Lewis acid sites studies

The spectrum of pyridine coordinatively bonded to the surface is very different from that of the pyridinium ion. As stated in the literature, peaks observed at 1450, 1490 and 1545 cm^{−1} correspond to Lewis, Brønsted and Lewis and Brønsted acid sites, respectively [39]. Fig. 5 presents FT-IR spectra of pyridine adsorbed samples.

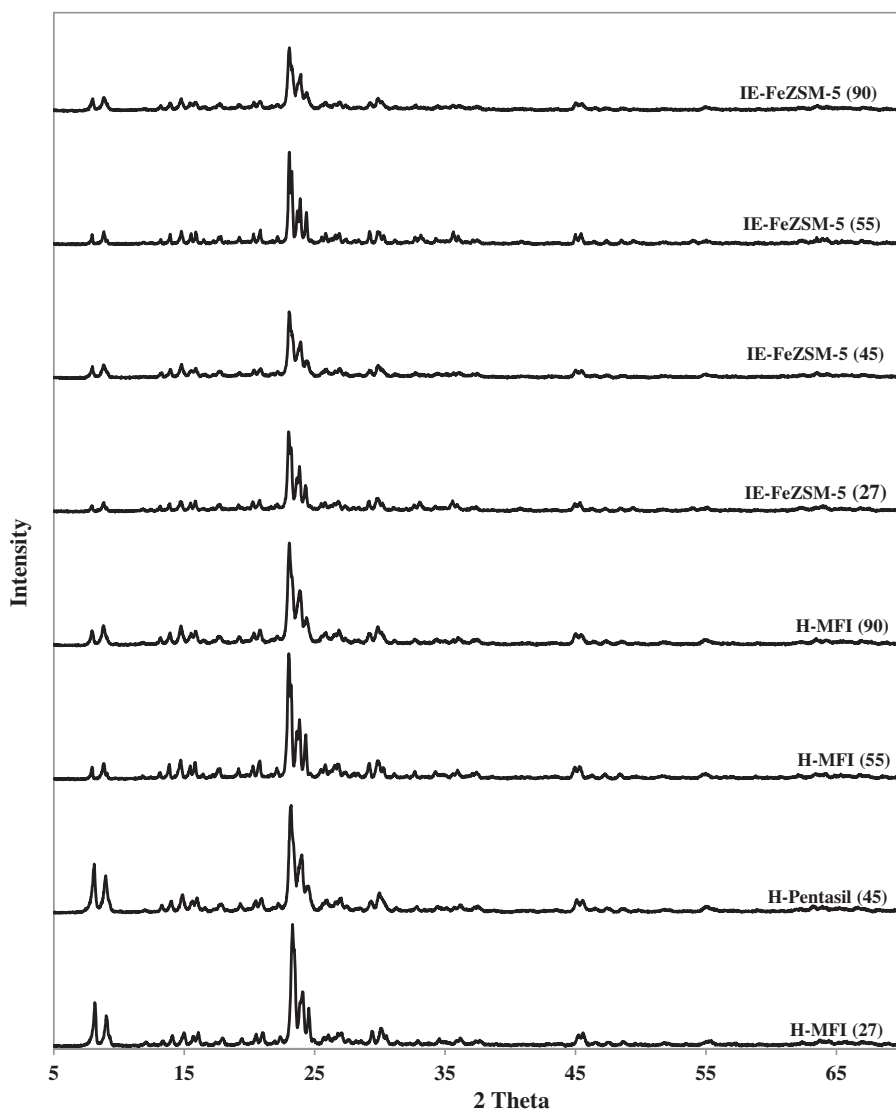


Fig. 2. X-ray diffraction patterns of all the catalysts and parent ZSM-5 zeolites.

Table 1

Nitrogen adsorption data and composition of prepared catalysts and parent zeolites.

Catalyst	Si/Al	Fe (wt%)	S_{BET} (m ² /g)	S_{μ} (m ² /g)	V_p (cm ³ /g)	V_{μ} (cm ³ /g)	d_{average} (nm) ^a
H-MFI (27)	12.3	7.5×10^{-4}	368.3	248.8	0.15075	0.13528	0.87
H-Pentasil (45)	41.5	7.5×10^{-4}	378.5	134.7	0.15074	0.07964	0.98
H-MFI (55)	19.0	7.5×10^{-4}	334.5	216.7	0.14141	0.14408	0.56
H-MFI (90)	43.8	7.5×10^{-4}	308.0	138.0	0.12561	0.09503	0.65
IE-FeZSM-5 (27)	12.4	6.6	336.6	240.0	0.14984	0.12804	0.92
IE-FeZSM-5 (45)	41.1	7.6	368.9	163.7	0.12555	0.08984	0.59
IE-FeZSM-5 (55)	18.6	8.1	302.6	197.4	0.10792	0.10792	0.60
IE-FeZSM-5 (90)	42.0	8.5	358.2	138.8	0.12585	0.09547	0.55

^a Calculated by Horvath–Kawazoe method.

Table 2

The intensities of spectra of pyridine-adsorbed samples at given wave numbers.

Catalysts	Absorbance (a.u.)		
	Lewis (L) at 1450 cm ⁻¹	B + L at 1490 cm ⁻¹	Brønsted (B) at 1545 cm ⁻¹
IE-FeZSM-5 (27)	0.006180	0.010972	0.005869
IE-FeZSM-5 (45)	0.006185	0.008823	0.005458
IE-FeZSM-5 (55)	0.004755	0.008213	0.005291
IE-FeZSM-5 (90)	0.011644	0.011335	0.011003

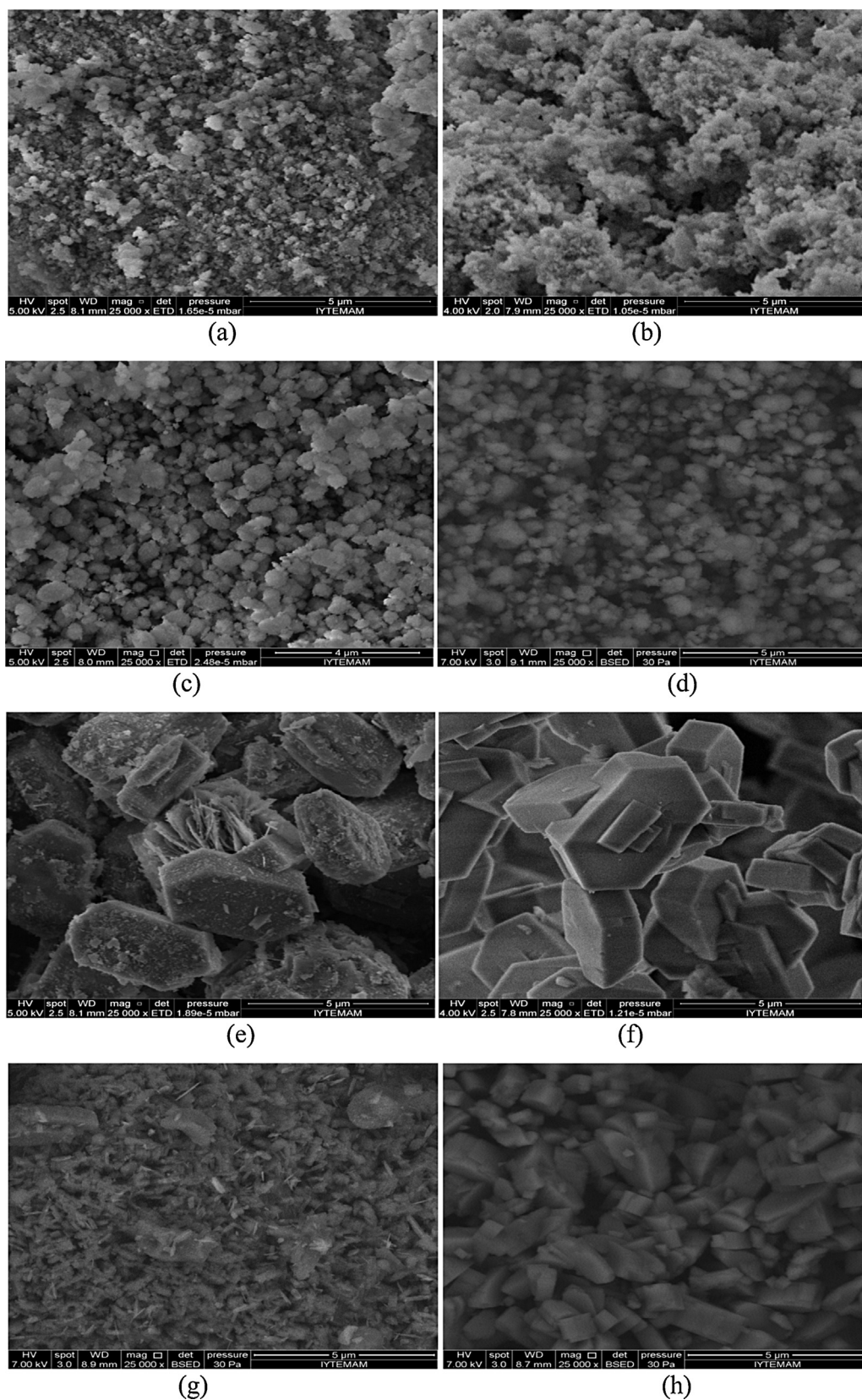


Fig. 3. SEM images of prepared catalysts and parent zeolites. (a) IE-FeZSM-5 (90), (b) H-MFI (90), (c) IE-FeZSM-5 (45), (d) H-Pentasil (45), (e) IE-FeZSM-5 (55), (f) H-MFI (55), (g) IE-FeZSM-5 (27), (h) H-MFI (27)

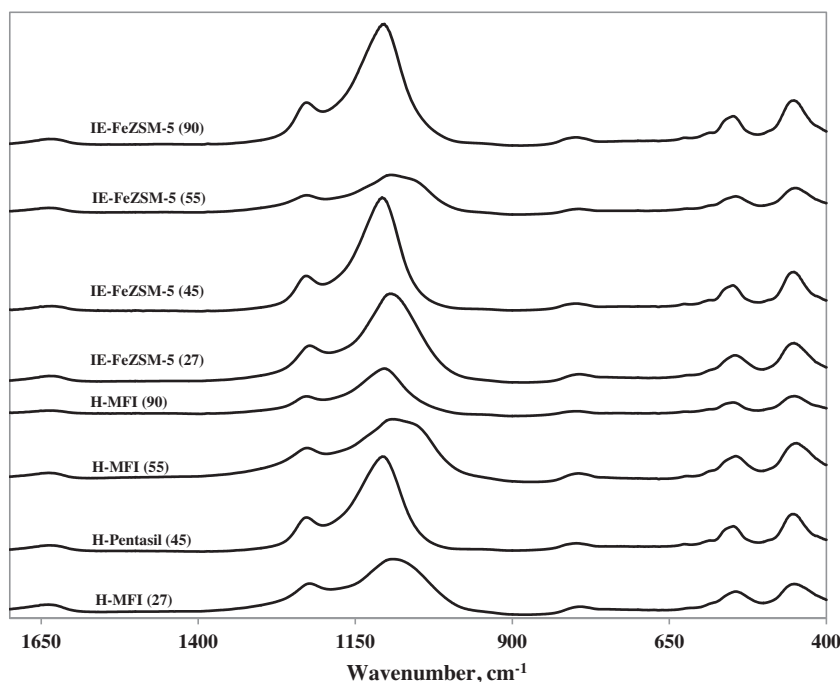


Fig. 4. FT-IR spectra of all parent ZSM-5 zeolites and the corresponding Fe-containing IE-FeZSM-5 catalysts prepared.

Table 2 shows the peak intensities of spectra of pyridine adsorbed samples at related wave numbers. As seen, IE-FeZSM-5 (90) catalyst has higher Lewis and Brønsted acidities than the other catalysts prepared. The catalysts have the following Brønsted acidity ordering:

$$\text{IE-FeZSM-5(90)} > \text{IE-FeZSM-5(27)} \\ > \text{IE-FeZSM-5(45)} > \text{IE-FeZSM-5(55)}$$

3.7. Catalyst screening tests for heterogeneous Fenton-like oxidation of acetic acid

The experiments of heterogeneous Fenton-like oxidation of acetic acid (AA) over prepared IE-FeZSM-5 catalysts and parent ZSM-5 zeolites were carried out by using 0.15 dm³ of aqueous acetic acid solution (0.1 g/dm³), 0.15 g catalyst and 8.35 mmol H₂O₂ solution (0.0557 M) at 333 K and at initial pH value of around 4. The reaction duration was taken to be 2 h.

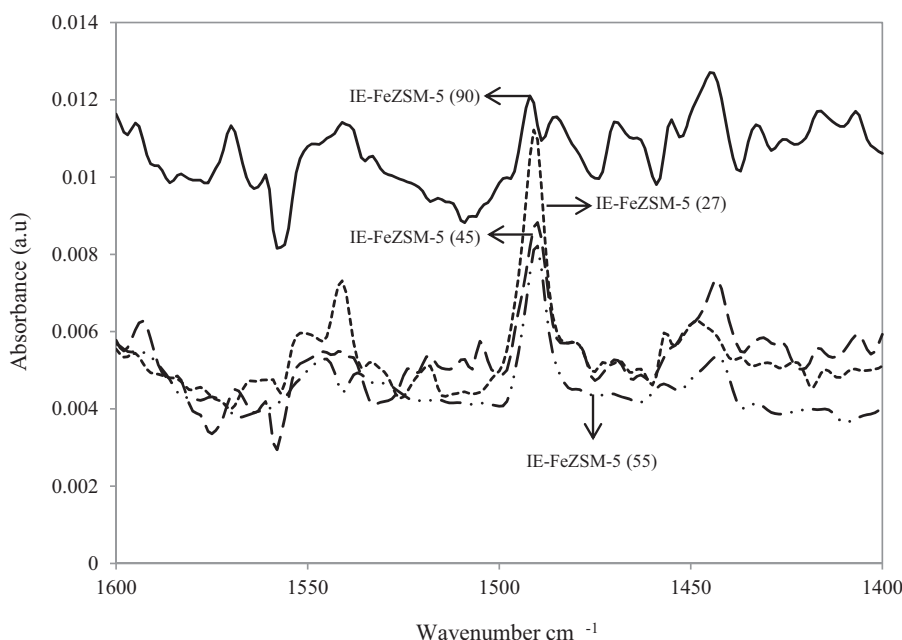


Fig. 5. Samples of FT-IR spectra of pyridine-adsorbed IE-FeZSM-5 catalysts.

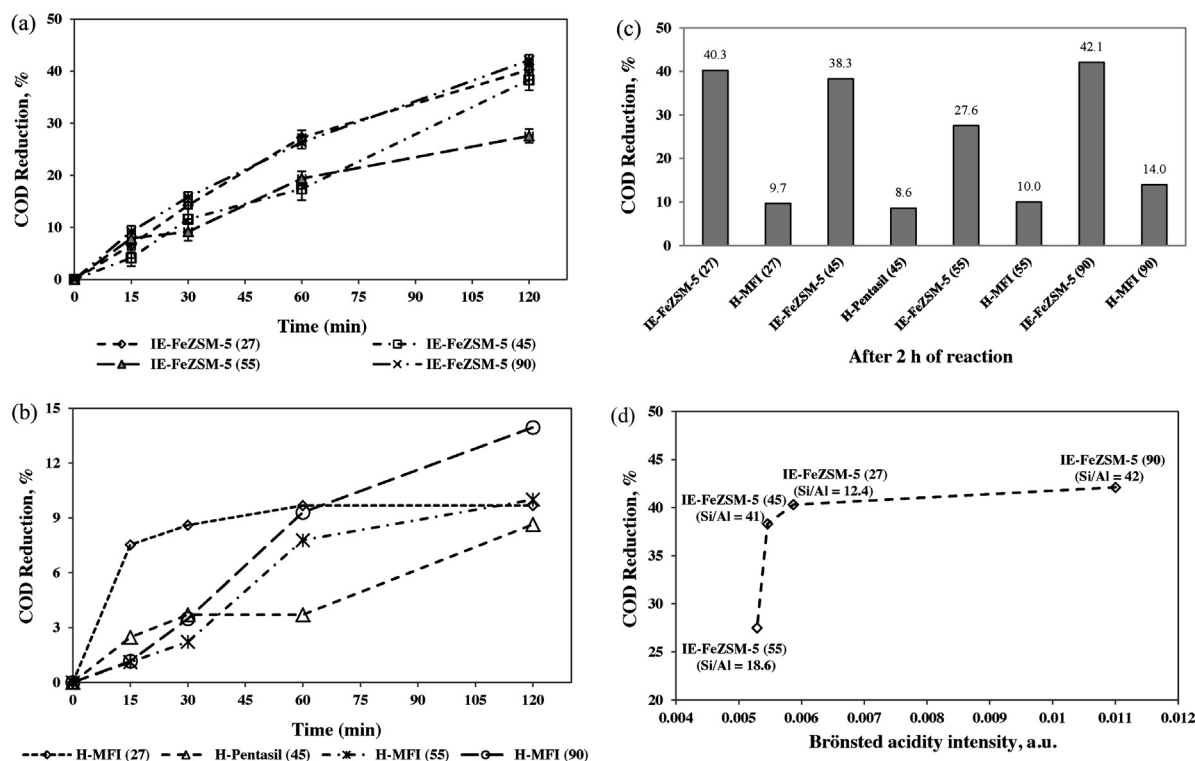


Fig. 6. The influence of catalyst type on COD reduction as a function of time at initial pH around 4.0: (a) COD reduction, %, as a function of time for IE-FeZSM-5 catalysts; (b) COD reduction, %, as a function of time for parent zeolites; (c) importance of iron loading to parent zeolite; (d) importance of Brønsted acidity (pH \approx 4.0, $\text{H}_2\text{O}_2/\text{AA} = 5.0$, catalyst amount = 0.15 g/0.15 dm³ solution, temperature = 333 K, acetic acid concentration = 0.10 g/dm³).

No noticeable acetic acid removal by adsorption on catalyst was obtained during heterogeneous Fenton-like oxidation experiments for all the catalysts synthesized. Destruction of an acid should be evaluated as an overall degradation process, involving the ultimate mineralization of both the acid and its intermediates which are produced during the oxidative degradation process. The most practical means of estimating this overall process is to monitor the reduction of chemical oxygen demand (COD).

3.7.1. Catalytic activities of different catalysts

Fig. 6 presents COD removal as a function of time for all the catalysts prepared and parent ZSM-5 zeolites. Fig. 6 also displays COD reduction measured after a reaction time of 2 h for all the catalysts studied. The standard deviation of the average of independent runs changed in the range of ± 1.00 to 2.21.

As seen in Fig. 6a, the highest chemical oxygen demand (COD) reduction of acetic acid was obtained to be 42.1% over IE-FeZSM-5 (90) catalyst after 2 h of reaction duration at initial pH around 4 (which is the natural pH value of acetic acid solution). The IE-FeZSM-5 (90) catalyst has the highest amount of iron among the catalysts tested. Si/Al ratio and Fe wt% of IE-FeZSM-5 (90) catalyst are 42.0 and 8.5%, respectively. This catalyst has the highest Lewis and Brønsted acidities, as well. The following ordering was obtained for COD reduction activity of the catalysts:

$$\text{IE-FeZSM-5(90)} > \text{IE-FeZSM-5(27)} \\ > \text{IE-FeZSM-5(45)} > \text{IE-FeZSM-5(55)}$$

Parent ZSM-5 zeolites showed lower activity (below a COD removal of 15%) in heterogeneous Fenton-like oxidation of acetic acid than those with iron loaded. As seen in Fig. 6b, when the parent ZSM-5 zeolites are compared with each other from the point of COD removal, H-MFI (90) shows the best catalytic activity (14%) among

the parent zeolites used. The following ordering was obtained for COD reduction activity of the parent zeolites after 2 h of reaction duration:

$$\text{H-MFI(90)} > \text{H-MFI(55)} > \text{H-MFI(27)} > \text{H-Pentasil(45)}$$

The catalytic activities of parent zeolites increased with iron loading. For instance, a COD removal of 14% was achieved in oxidation of acetic acid by Fenton reaction with H-MFI (90) zeolite. When it was loaded with iron (8.5 wt%), a COD removal of 42.1% could be obtained. An iron loading of 8.1 wt% to H-MFI (55) increased the COD removal from 10 to 27.6%. Fig. 6c presents COD reduction after a reaction time of 2 h for all the catalysts tested at initial pH around 4.0. It clearly shows the importance of iron loading to ZSM-5 zeolites in heterogeneous Fenton-like oxidation of acetic acid. Fig. 6d presents COD removal as a function of Brønsted acidity. As seen, COD removal increases with the increase in Brønsted acidity of the catalyst. Brønsted acidity of the catalyst is more significant in catalytic activity than its iron content. For instance, IE-FeZSM-5 (27) catalyst has a higher COD removal than that for IE-FeZSM-5 (55) catalyst even though iron loading of the latter is much higher than IE-FeZSM-5 (27) catalyst.

Amount of iron loss from catalyst into the solution was determined by measuring the iron concentration in the solution after a reaction time of 2 h, with atomic absorption spectrophotometer (Varian 10 plus). Iron leached was measured in the range of 0.06–0.25 mg/dm³ (in terms of iron loss of 0.09–0.41%). For all the catalysts, the iron leaching is negligibly low and well below the EU directives (<2.0 mg/dm³).

Activity screening runs clearly indicates that IE-FeZSM-5 (90) catalyst is the most active catalyst in the heterogeneous Fenton-like oxidation of acetic acid. The effects of temperature, initial concentration of acetic acid, solution pH, amounts of H_2O_2 and catalyst were investigated on degradation of acetic acid over this catalyst.

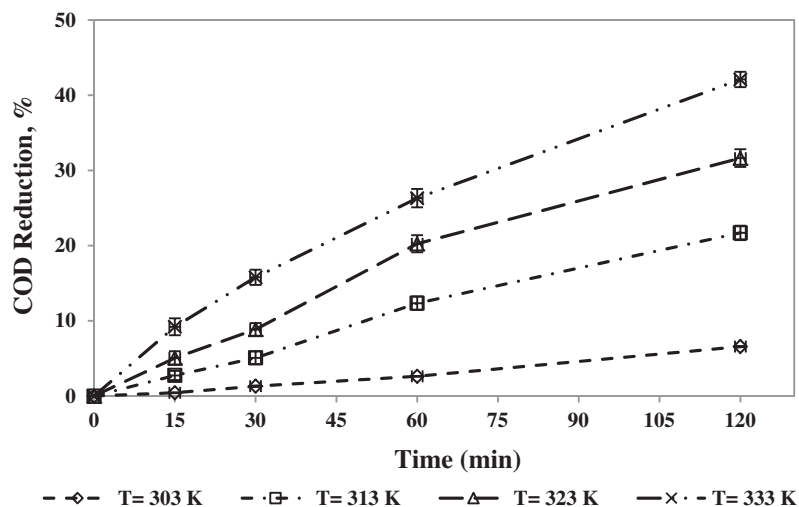


Fig. 7. Effect of temperature on heterogeneous Fenton-like oxidation of acetic acid over IE-FeZSM-5 (90) catalyst at initial pH around 4 ($\text{pH} \approx 4$, $\text{H}_2\text{O}_2/\text{AA}=5$, catalyst amount = $0.15 \text{ g}/0.15 \text{ dm}^3$ solution, acetic acid concentration = $0.1 \text{ g}/\text{dm}^3$).

3.7.2. The effect of temperature on heterogeneous Fenton-like oxidation

The effect of temperature on heterogeneous Fenton-like oxidation of acetic acid was investigated at four different temperatures 303, 313, 323 and 333 K under the following reaction conditions over IE-FeZSM-5 (90) catalyst: Initial acetic acid concentration of $0.1 \text{ g}/\text{dm}^3$, catalyst amount $0.15 \text{ g}/0.15 \text{ dm}^3$ acetic acid solution ($0.1 \text{ g catalyst}/\text{dm}^3$ solution), initial pH around 4 and H_2O_2 amount of 8.35 mmol . The results were presented with error bars in Fig. 7 as COD reduction as a function of time. COD reduction was enhanced with the increase in temperature, being 6.6, 21.7, 31.6 and 42.1% (standard deviation = ± 0.06 – 1.22) for temperatures of 303, 313, 323 and 333 K, respectively.

The initial COD removal rate in degradation of acetic acid increased with an increase in temperature. This was expected due to the exponential dependency of the reaction rate constant on temperature. At high temperatures, COD reduction rate decreased because of the accelerated decomposition of H_2O_2 into oxygen and water [40]. For this reason, 333 K seems to be a good temperature for heterogeneous Fenton-like oxidation of acetic acid over IE-FeZSM-5 (90) catalyst. During the experiments, pH of the solution did not change, it remained constant around 4.

In literature, following results have been reported in catalytic wet peroxide oxidation (CWPO) of acetic acid. A conversion of 20% could be achieved in CWPO of acetic acid at 343 K over a FeZSM-5 zeolite catalyst [16]. A TOC removal of 63% could be obtained in CWPO of acetic acid at 363 K over a Cu^{+2} -NaY zeolite [21]. Acetic acid could be oxidized only 31% in catalytic wet air oxidation of acetic acid at 333 K over a Pt/SiO_2 catalyst [22].

The catalyst stability to leaching iron ions did not change significantly. Iron leaching was in the range of 0.19 – $0.27 \text{ mg}/\text{dm}^3$ (in terms of iron loss of 0.28 – 0.39%), which is well below the EU directives. Hence, it is reasonable to oxidize acetic acid in the presence of IE-FeZSM-5 (90) catalyst at 333 K.

3.7.3. The effect of initial concentration of acetic acid on heterogeneous Fenton-like oxidation

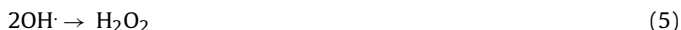
The effect of initial concentration on heterogeneous Fenton-like oxidation of acetic acid was investigated at six different initial concentrations of acetic acid of $0.01 \text{ g}/\text{dm}^3$ (10 ppm), $0.025 \text{ g}/\text{dm}^3$ (25 ppm), $0.075 \text{ g}/\text{dm}^3$ (75 ppm), $0.1 \text{ g}/\text{dm}^3$ (100 ppm) and $0.125 \text{ g}/\text{dm}^3$ (125 ppm) under the following reaction conditions over IE-FeZSM-5 (90) catalyst: Catalyst amount $0.15 \text{ g}/0.15 \text{ dm}^3$

acetic acid solution, temperature of 333 K, initial pH around 4 and H_2O_2 amount of 8.35 mmol . Obtained results were presented in Fig. 8a with error bars.

As seen from Fig. 8a, COD reduction decreased with increasing initial concentration of acetic acid, being 73.2, 58.9, 48.6, 42.1 and 34.9% (standard deviation ± 1.00 – 2.49) for initial concentrations of 0.01, 0.025, 0.075, 0.1 and $0.125 \text{ g}/\text{dm}^3$ for IE-FeZSM-5 (90), respectively, after a reaction time of 2 h. The highest COD removal could be achieved at $0.01 \text{ g}/\text{dm}^3$ of initial concentration of acetic acid. During the experiments, pH value of the solution remained constant around 4. Fig. 8b presents COD reduction and H_2O_2 consumption percentages measured after 2 h of reaction. Oxidation of acetic acid with H_2O_2 is given by the equation below:



The stoichiometric ratio of H_2O_2 to acetic acid is 4. When acetic acid at initial concentration of $0.125 \text{ g}/\text{dm}^3$ was used for oxidation, the ratio of H_2O_2 to AA is equal to the stoichiometric ratio and H_2O_2 consumption percentage after 2 h of reaction is 67%. The H_2O_2 consumption increases from 67 to 76% with the decrease in initial concentration of acetic acid from 0.125 to $0.025 \text{ g}/\text{dm}^3$. A decrease from 76 to 73% in H_2O_2 consumption is observed with the change in initial concentration of acetic acid from 0.025 to $0.01 \text{ g}/\text{dm}^3$. This result can be explained by the scavenging effect of H_2O_2 or by recombination of OH^\cdot radicals at high $\text{H}_2\text{O}_2/\text{AA}$ ratios:



Iron loss increased from $0.15 \text{ mg}/\text{dm}^3$ (0.22%) to $0.32 \text{ mg}/\text{dm}^3$ (0.46%) with increasing initial concentration of acetic acid (AA) from 0.010 to $0.125 \text{ g}/\text{dm}^3$ due to the increasing acidity of reaction solution. Nevertheless, iron loss is still below the EU directives ($<2 \text{ mg}/\text{dm}^3$).

3.7.4. The effect of catalyst amount on heterogeneous Fenton-like oxidation

The effect of catalyst amount on heterogeneous Fenton-like oxidation of acetic acid was studied at four different catalyst amounts of 0.1, 0.15, 0.2 and 0.3 g for 0.15 dm^3 of acetic acid solution under the following reaction conditions: Initial acetic acid concentration of $0.1 \text{ g}/\text{dm}^3$, temperature of 333 K, initial pH around 4 and H_2O_2 amount of 8.35 mmol . Obtained results were presented in Fig. 9a with standard deviation range of ± 0.72 – 2.13 .

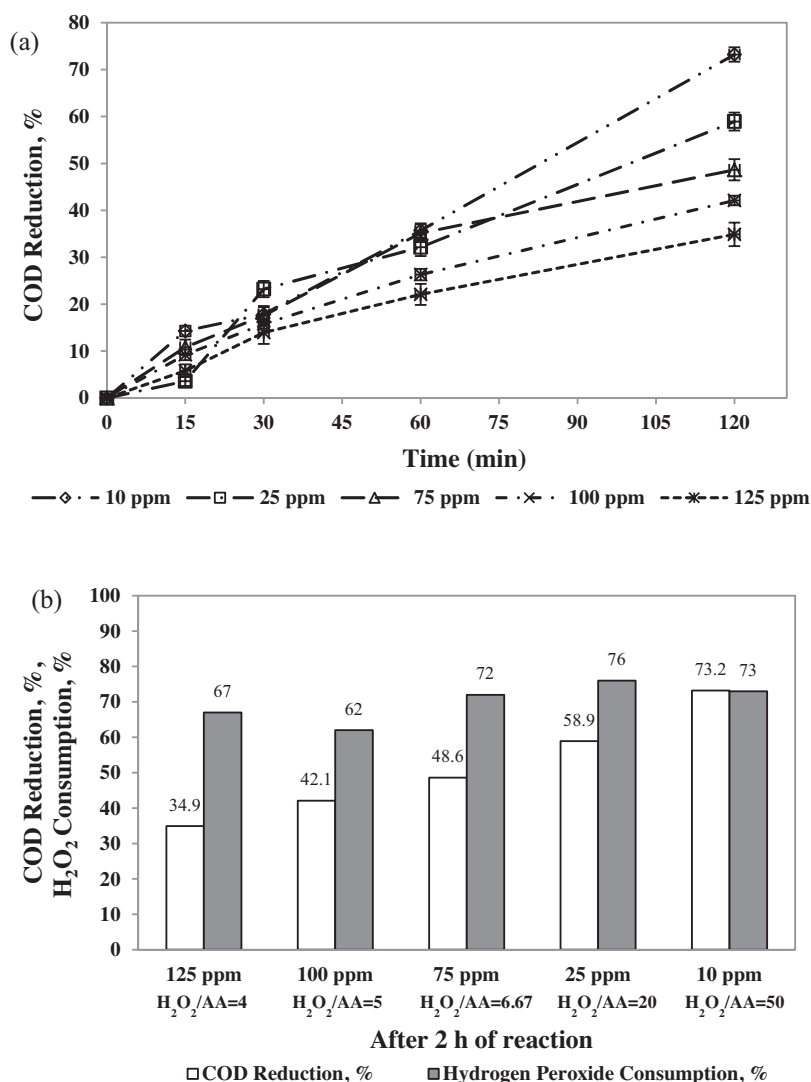


Fig. 8. Effect of initial concentration of acetic acid on heterogeneous Fenton-like oxidation of acetic acid over IE-FeZSM-5 (90) catalyst at initial pH around 4: (a) COD reduction, %, as a function of time; (b) COD reduction, %, and H₂O₂ consumption, %, after 2 h of reaction (pH \approx 4, catalyst amount = 0.15 g/0.15 dm³ solution, temperature = 333 K).

As expected, COD reduction increased with increasing amount of catalyst. When the catalyst loading is enhanced from 0.1 to 0.2 g, COD reduction raised from 35.9 to 42.1 to 50.5% after a reaction time of 2 h. Obtained results could be explained by the increasing number of active centers which were effective on degradation of acetic acid, with increasing catalyst amount. However, COD reduction did not show a big difference with the increase in catalyst amount from 0.2 to 0.3 g (50.5% at 0.2 g catalyst and 50.6% at 0.3 g catalyst). It indicated that 0.2 g of catalyst was the sufficient catalyst amount for COD reduction for IE-FeZSM-5 (90) catalyst in the studied range.

As the catalyst amount increased from 0.1 through 0.15 to 0.2 g of catalyst, initial COD removal rate of the reaction increased. However, as the catalyst amount increased to a higher value (0.3 g), a competition begins between the particles for the reactant molecules and the initial reaction rate remained almost constant. During the experiments, pH value of the solution remained constant around 4. Fig. 9b presents also H₂O₂ consumption measured after 2 h of reaction at different catalyst amounts. H₂O₂ consumption increased with increasing amount of catalyst. When catalyst amount was tripled from 0.1 to 0.3 g, H₂O₂ amount consumed was almost doubled (from 50 to 90%). This result indicated that the number of active sites in the catalyst increased with the amount of catalyst employed in the reaction. No significant change in COD

removal was observed when catalyst amount increased from 0.2 to 0.3 g. This result shows that small organic molecular fragments which are not completely mineralized are produced under the oxidation conditions used. Iron loss was below the EU directives and was in a range of 0.22–0.29 mg/dm³ (in terms of iron loss; 0.32–0.42%).

3.7.5. Effect of solution pH on heterogeneous Fenton-like oxidation

The effect of solution pH on heterogeneous Fenton-like oxidation of acetic acid was studied at two different pH values of 7 and 4 under the following reaction conditions over IE-FeZSM-5 (90) catalyst: Initial acetic acid concentration of 0.1 g/dm³, temperature of 333 K, the amount of catalyst 0.2 g/0.15 dm³ acetic acid solution and H₂O₂ amount of 8.35 mmol. The solution initial pH was regulated with 0.1 M NaOH at the beginning of the experiment with pH 7. Fig. 10 shows the results with a standard deviation range of ± 1.76 –3.34.

The increase in solution pH from 4 to 7 affected negatively the COD reduction in degradation of acetic acid. When the solution pH value decreased from 7 to 4, COD reduction increases from 20.9 to 50.5%, respectively, after a reaction time of 2 h. It is clearly understood that initial pH around 4 value is the effective pH value for

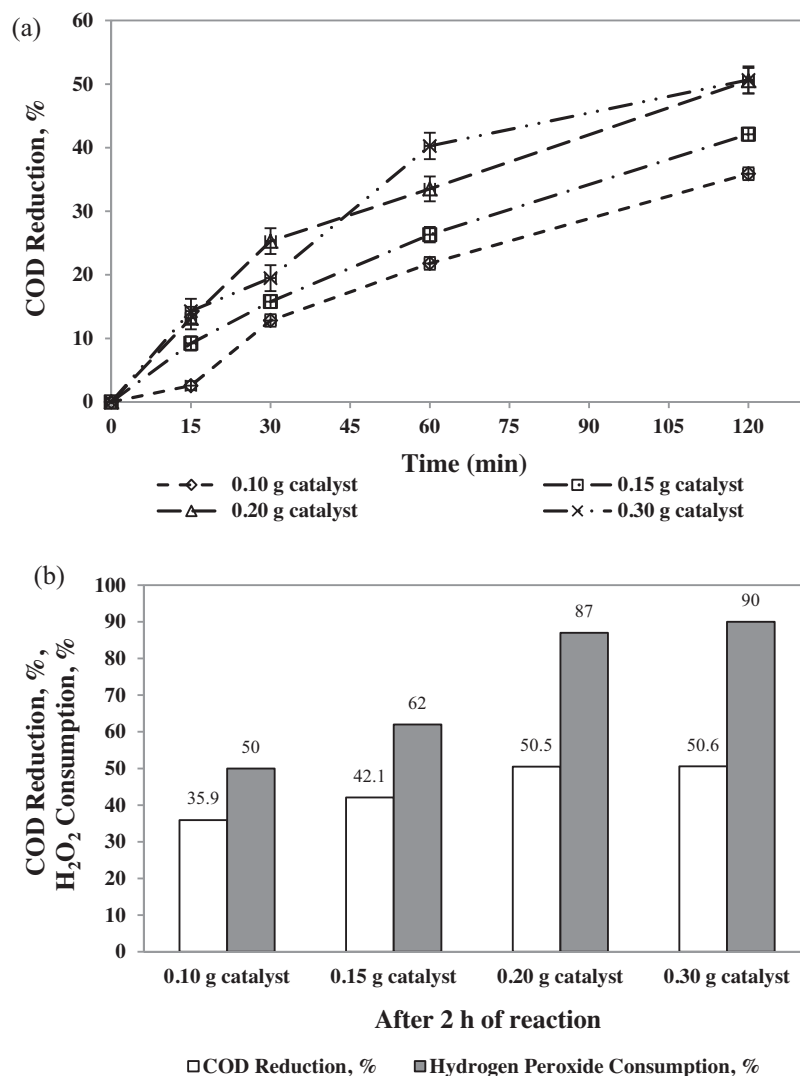


Fig. 9. Effect of catalyst amount on heterogeneous Fenton-like oxidation of acetic acid over IE-FeZSM-5 (90) catalyst at initial pH around 4: (a) COD reduction, %, as a function of time; (b) COD reduction, %, and H₂O₂ consumption, %, after 2 h of reaction (pH ≈ 4, H₂O₂/AA = 5, temperature = 333 K, acetic acid concentration = 0.1 g/dm³).

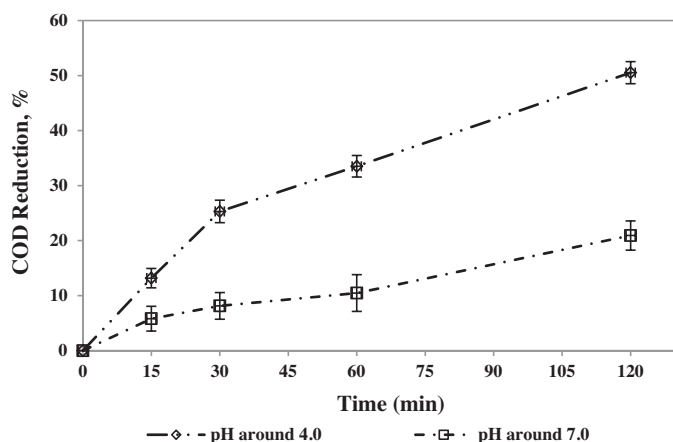


Fig. 10. Effect of pH values on heterogeneous Fenton-like oxidation of acetic acid over IE-FeZSM-5 (90) catalyst (H₂O₂/AA = 5, catalyst amount = 0.2 g/0.15 dm³ solution, temperature = 333 K, acetic acid concentration = 0.1 g/dm³).

COD reduction in acetic acid degradation over the catalyst studied. Initial rate was much lower at pH around 7 than that at pH around 4. H₂O₂ consumption is doubled after a reaction time of 2 h at pH around 4 from 42% (at pH 7) to 87%.

It should be kept in mind that degradation of acetic acid was accelerated in the presence of IE-FeZSM-5 (90) catalyst which had the highest Brønsted acidity.

In literature, similar results have been reported in catalytic wet peroxide oxidation (CWPO) of carboxylic acids over a FeZSM-5 catalyst [16], in mineralization of acetic and oxalic acid by using wet peroxide oxidation (WPO) [41], in radiolysis of acetic acid in aqueous solution [42] and in homogeneous photo catalytic mineralization of acetic acid [43].

As expected, iron leaching was higher at pH 4 (0.26 mg/dm³) than that at pH 7 (0.19 mg/dm³). However, iron leached was much lower than 2 mg/dm³.

3.7.6. Effect of H₂O₂ addition on heterogeneous Fenton-like oxidation

The effect of H₂O₂ addition on heterogeneous Fenton-like oxidation of acetic acid was investigated at four different H₂O₂ concentrations of 3.34 mmol (0.0223 M, n_{H2O2}/n_{AA} = 2), 6.68 mmol

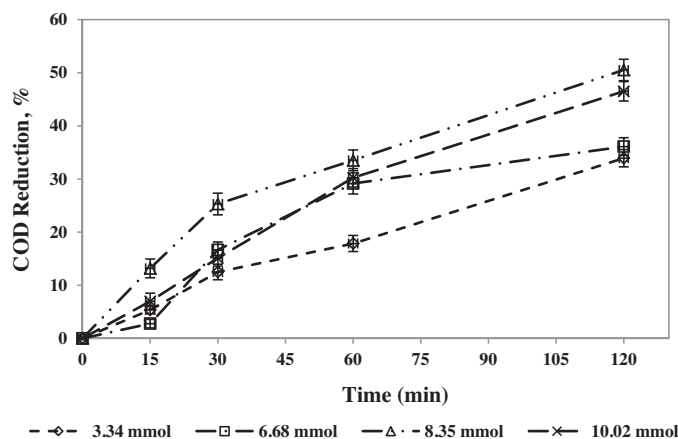


Fig. 11. Effect of hydrogen peroxide addition on heterogeneous Fenton-like oxidation of acetic acid over IE-FeZSM-5 (90) catalyst at initial pH around 4 ($\text{pH} \approx 4$, catalyst amount = 0.2 g/0.15 dm³ solution, temperature = 333 K, acetic acid concentration = 0.1 g/dm³).

(0.0445 M, $n_{\text{H}_2\text{O}_2}/n_{\text{AA}} = 4$), 8.35 mmol (0.0557 M, $n_{\text{H}_2\text{O}_2}/n_{\text{AA}} = 5$) and 10.02 mmol (0.0668 M, $n_{\text{H}_2\text{O}_2}/n_{\text{AA}} = 6$) under the following reaction conditions over IE-FeZSM-5 (90) catalyst: Initial acetic acid concentration of 0.1 g/dm³, the amount of catalyst 0.2 g/0.15 dm³ acetic acid solution, pH around 4 and temperature of 333 K. The obtained results were presented in Fig. 11 with a standard deviation range of ± 0.75 –2.04.

As seen from Fig. 11, increasing the concentration of H₂O₂ from 3.34 to 6.68 and to 8.35 mmol affected positively the COD removal. COD removal was enhanced from 33.9 through 36.1 to 50.5%, respectively. This result is expected, because more OH[•] radicals are produced with increasing amount of H₂O₂. Also, during the experiments, pH value of the solution remained almost constant around 4. The highest COD reduction was obtained to be 50.5% with 8.35 mmol H₂O₂ after 2 h of oxidation over IE-FeZSM-5 (90) catalyst. The highest initial COD reduction rate was also achieved at this initial H₂O₂ amount. The increase in amount of H₂O₂ from 8.35 to 10.02 mmol dropped the COD reduction from 50.5 to 46.5% after 2 h of reaction. This result can be attributed to the reaction between H₂O₂ and generated hydroxyl radicals (OH[•]) to produce hydroperoxyl radicals (HO₂[•]) which is called as scavenging effect of H₂O₂ (Eq. (6)).

Oxidation potential of HO₂[•] radicals is much smaller than that of the OH[•] species. When 10.02 mmol H₂O₂ was added to the reaction mixture, the COD reduction and the initial rate of reaction were decreased because of the formation of less reactive HO₂[•] radicals. H₂O₂ consumption increased from 77 through 80 to 87% with the change in H₂O₂ amount from 3.34 through 6.68 to 8.35 mmol. However, H₂O₂ consumption dropped to 82% with the increase in H₂O₂ amount from 8.35 to 10.02 mmol. The latter H₂O₂ amount was rather excess (1.5 times of the stoichiometric ratio). 8.35 mmol of H₂O₂ seems to be sufficient for oxidation of acetic acid under the studied conditions.

Iron leached into the solution was in the range of 0.16–0.25 mg/dm³ (in terms of iron loss; 0.23–0.38%), which was much lower than 2 mg/dm³, after a reaction time of 2 h.

3.7.7. The optimum conditions for heterogeneous Fenton-like oxidation

In the light of the experiments done in the parametric study, the optimum conditions were selected for heterogeneous Fenton-like oxidation of acetic acid for an initial concentration of 0.1 g/dm³. IE-FeZSM-5 (90) catalyst was found to be the best catalyst and 0.2 g of this catalyst was sufficient for oxidation of acetic acid. The optimum reaction temperature was determined as 333 K. The optimum

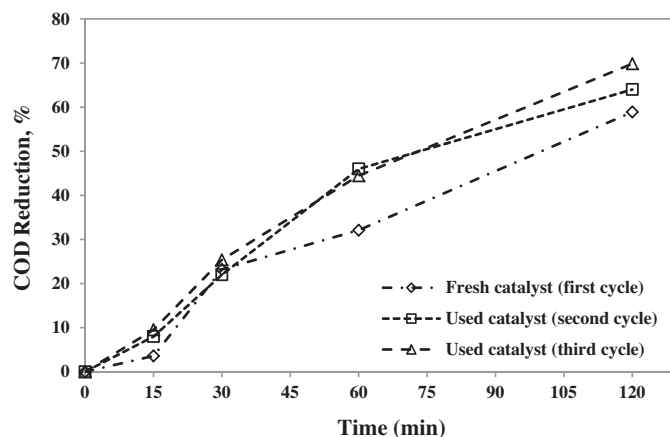


Fig. 12. Recycling of IE-FeZSM-5 (90) catalyst in the oxidation of acetic acid.

pH value was around 4. The optimum hydrogen peroxide concentration was determined to be 8.35 mmol/0.15 dm³ solution. A COD removal of 50.5% and a H₂O₂ consumption of 87% were achieved under these optimum conditions.

When heterogeneous Fenton-like oxidation of acetic acid was investigated under the optimum conditions for 0.025 g/dm³ of initial acetic acid concentration ($n_{\text{H}_2\text{O}_2}/n_{\text{AA}} = 20$), COD removal reached to 55.74% after 2 h of oxidation, due to the low initial concentration of acetic acid.

3.7.8. Stability and recycling of the catalyst on heterogeneous Fenton-like oxidation

Catalyst stability is one of the most significant parameters for a heterogeneous catalytic system. The re-use of the catalyst is of vital importance in the industry. For this purpose, the stability of the catalyst IE-FeZSM-5 (90) was investigated under the following conditions: 0.15 dm³ of 0.025 g/dm³ acetic acid solution, 0.2 g of IE-FeZSM-5 (90) catalyst, 8.35 mmol of H₂O₂, a reaction temperature of 333 K and initial solution pH of around 4.

Firstly, fresh catalyst was used for degradation of acetic acid in heterogeneous Fenton-like oxidation (first cycle). Secondly, to recover the catalyst after 2 h of oxidation, the final effluent was filtered, dried, washed with ethanol and then water. Later on, this catalyst was calcined according to the procedure given in catalyst preparation section. Acetic acid was degraded over this used catalyst for 2 h (second cycle) and then after the same regeneration procedure, it was used in the degradation of acetic acid (third cycle).

Catalyst performances reached in terms of COD removal are presented in Fig. 12. Interestingly, COD removal increased with the number of cycle. That is, a COD removal of 58.9% was obtained with the fresh catalyst (first cycle). COD removal reached 64% in the second cycle and finally a COD removal of 69.8% was achieved in the third used of the catalyst (third cycle). Washing with ethanol and calcination procedure may cause an improvement in the surface area and pore volume of the catalyst allowing acetic acid molecules to reach easily into the active centers in the catalyst.

Iron leaching enhanced a little with the cycle number of the catalyst from 0.17 to 1.67 mg/dm³ (in terms of iron loss from 0.25 to 2.5%), being still below the EU directives (<2 mg/dm³).

3.7.9. Kinetic study on heterogeneous Fenton-like oxidation of acetic acid

In heterogeneous Fenton-like oxidation experiments, the reaction mixture was stirred vigorously at around 290 rpm. The external diffusion resistance between the bulk solution and the catalyst surface could be eliminated. Because according to Hougen's criterion [44], the ratio of the acetic acid (AA) concentration difference

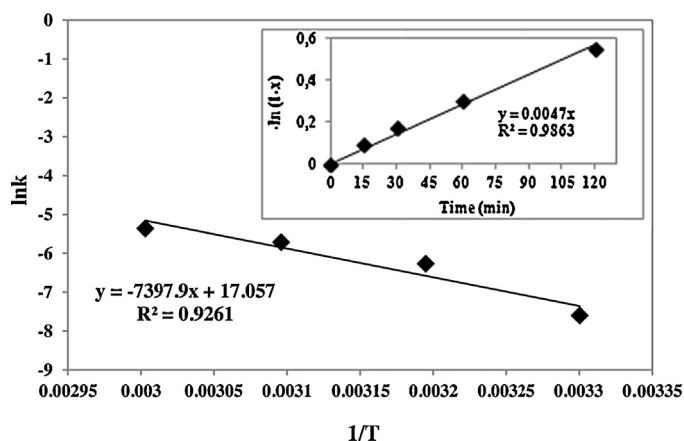


Fig. 13. $\ln k$ versus $1/T$ dependence for COD reduction of acetic acid (inset: $-\ln(1-x)$ vs time dependence).

between the bulk solution and the catalyst surface, $(C_b - C_s)$, to bulk concentration, (C_b) , $(C_b - C_s)/C_b$ was calculated to be 1.44×10^{-4} which was much smaller than 0.1. On the other hand, internal diffusion resistance was also negligible because Thiele modulus, $\Phi_s = \frac{1}{3} r_s \sqrt{k_1 \rho_p / D_e}$ where r_s = catalyst pellet radius, ρ_p = catalyst pellet density and D_e = effective diffusivity of AA in solution, was calculated [44,45] to be 5.82×10^{-6} which was smaller than 1/3 which indicated that effectiveness factor could be taken as unity.

First-order kinetics in acetic acid oxidation was reported by Shende et al. [46], Gomes et al. [47], Heintz et al. [48] and by Klinghoffer et al. [49]. For this reason, experimental data were tested for first-order kinetics:

$$-\ln(1-x) = k * t \quad (10)$$

where k is the reaction rate constant, t is the time and x is the obtained conversion (here COD removal) at time t . Fig. 13 (as inset) indicates the plot obtained by using the COD, %, vs time data for the heterogeneous Fenton-like oxidation experiment done with 8.35 mmol H_2O_2 ($H_2O_2/AA=5$) for initial concentration of acetic acid of 0.1 g/dm³ at 333 K. That plot was drawn for different reaction temperatures and reaction rate constant was calculated for each temperature. Table 3 presents the results. On the other hand, the validity of the first-order kinetic model was checked for the experimental data of all the operation variables studied and the results were presented in Table 3. High regression coefficients indicate that heterogeneous Fenton-like oxidation of acetic acid fits first-order kinetics.

According to Arrhenius equation ($k = A e^{-E/RT}$, where A is the frequency factor and R is universal gas constant (8.314 J/mol K)), activation energy (E) was calculated to be 61.5 kJ/mol from the slope of the straight line obtained by plotting $\ln k$ versus $1/T$ (Fig. 13).

Acetic acid oxidation can be expressed by the following equation:

$$-r_{AA} = 2.56 \times 10^7 e^{-61.5/RT} C_{AA}$$

Activation energy was found to be 100.5 kJ mol⁻¹ by Gallezot et al. [50] in catalytic wet air oxidation (CWAO) of AA over a carbon supported ruthenium catalyst. It was obtained to be 100 kJ mol⁻¹ by Barbier et al. [51] in CWAO of AA over a Ru/CeO₂ catalyst and to be 175 ± 13 kJ mol⁻¹ by Gomes et al. [52] in CWAO of AA over a 1% Pt/Carbon catalyst and by Shende et al. [46] as 178 kJ mol⁻¹ in wet oxidation of acetic acid on cupric sulfate.

The activation energy found in this study is lower than those in the literature on acetic acid. The lower value of activation energy supports the idea that how active the IE-FeZSM-5 (90) catalyst used

Table 3

Reaction rate constants and regression coefficients at different operating conditions.

	k (min ⁻¹)
Effect of temperature (K) (Fig. 7)	
303	0.0005 ($R^2 = 0.9783$)
313	0.0019 ($R^2 = 0.9934$)
323	0.0033 ($R^2 = 0.9885$)
333	0.0047 ($R^2 = 0.9863$)
Effect of initial concentration of AA (ppm) (Fig. 8)	
10	0.0101 ($R^2 = 0.9553$)
25	0.0072 ($R^2 = 0.9805$)
75	0.0059 ($R^2 = 0.9690$)
100	0.0047 ($R^2 = 0.9863$)
125	0.0038 ($R^2 = 0.9783$)
Effect of catalyst amount (g) (Fig. 9)	
0.10	0.0038 ($R^2 = 0.9852$)
0.15	0.0047 ($R^2 = 0.9863$)
0.20	0.0063 ($R^2 = 0.9435$)
0.30	0.0065 ($R^2 = 0.9244$)
Effect of pH (Fig. 10)	
4	0.0063 ($R^2 = 0.9435$)
7	0.0020 ($R^2 = 0.9460$)
Effect of H_2O_2 addition (mmol) (Fig. 11)	
3.34	0.0035 ($R^2 = 0.9902$)
6.68	0.0042 ($R^2 = 0.8940$)
8.35	0.0063 ($R^2 = 0.9435$)
10.02	0.0054 ($R^2 = 0.9927$)
Recycling of catalyst (Fig. 12)	
First cycle	0.0072 ($R^2 = 0.9805$)
Second cycle	0.0088 ($R^2 = 0.9839$)
Third cycle	0.0099 ($R^2 = 0.9973$)

in this study is in the heterogeneous Fenton-like oxidation of acetic acid.

4. Conclusions

In this study, heterogeneous Fenton-like oxidation of acetic acid was studied in the presence of iron containing ZSM-5 zeolite catalyst. The higher the Brønsted acidity, the more active the ZSM-5 catalyst was achieved in the heterogeneous Fenton-like oxidation of AA. Degradation of AA was accelerated in acidic medium with the increase in temperature, H_2O_2 and catalyst amount. It could be possible to degrade AA with a COD removal of 50.5% which was a rather good abatement for AA when compared with the degradation values given in the literature. For this reason, it can be said that oxidation by heterogeneous Fenton-like reaction can be a promising advanced oxidation technology for degradation of acetic acid.

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